

## A REVIEW ON PROCESS PARAMETERS ASSOCIATED WITH CONSTITUTIVE MODELLING OF SHAPE MEMORY ALLOYS-2

M. BABURAM<sup>1</sup>, DHEERAJ K GARA<sup>2</sup>, K. DAMODHAR<sup>3</sup> & K. GURUBRAHMAM<sup>4</sup>

<sup>1,3</sup>Undergraduate Student, Department of Mechanical Engineering, Chaitanya Bharathi Institute of Technology,  
Hyderabad, India

<sup>2</sup>Project Manager, <sup>2</sup>Vsky Aerospace Technologies, Hyderabad, India

<sup>4</sup>Assistant Professor, Department of Mechanical Engineering, Chaitanya Bharathi Institute of Technology, Hyderabad, India

### ABSTRACT

*In extension to the last review on constitutive models for shape memory alloys (SMAs), we can realize that most of the parameters involved in developing the constitutive model depend on processing techniques and hence the present paper emphasizes this context. A comprehensive literature review from the previous observations will be made available in the present paper along with the research gaps identified for exploring these SMAs towards aerospace and automotive applications.*

**KEYWORDS:** Shape Memory Alloy, Process Parameters & Constitutive Model

**Received:** Sep 01, 2019; **Accepted:** Sep 20, 2019; **Published:** Oct 10, 2019; **Paper Id.:** IJMPERDDEC201913

### INTRODUCTION

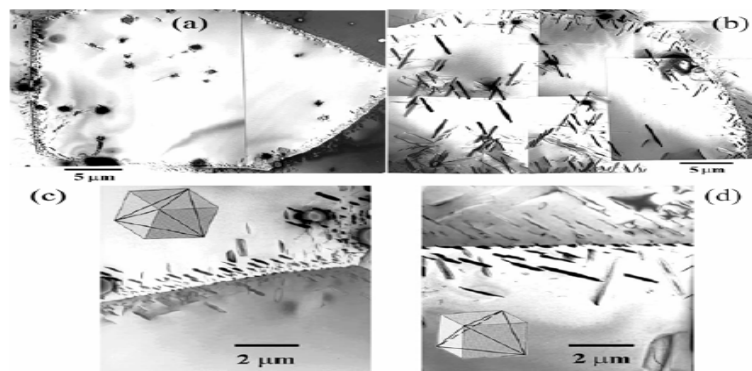
Over the last few decades shape memory alloys have become the most trending materials because of its unique properties namely shape memory effect (SME) and pseudo elasticity that ensemble most of the societal challenges. However, many micro, micro-macro, macro constitutive models were developed to understand these materials' behavior. But the present paper emphasizes the influence of processing parameters on Nitinol exhibiting SME. From our previous paper one can realize that most of the micro and macroscale parameters depend upon the processing parameters, hence, emphasize on the processing parameters will be made in the present context. These understandings of processing parameters enable us to choose different manufacturing routes, composition dependence and processing environments influencing the range of super elasticity and SME. This understanding of influence of parameters allow us to develop products amenable to aerospace and automotive applications without altering the property of SME instead improving the strength to weight ratio, range of transition temperatures and corrosion properties.

### Multi Stage Transformation (MST)

The traditional basic view of phase transformations in Ni-Ti alloys includes only one-stage cubic austenite (B2) to monoclinic (B19') martensite transformation, however, the influence of cold working associated with high density of dislocations (H. Morawiec, 1995) (Morawiec, Stroz, Goryczka, & Chrobak, 1996) (Morawiec D. C., 2003) and the presence of Ni-rich precipitates in Ni-Ti alloys contribute to a more complex two-stage, three-stage or even four-stage transformations, collectively termed as 'multiple stage transformation' (Carroll, 2004).

It is now inevitable that the presence of dislocation substrates or precipitates into the Ni-Ti matrix can act as hindrances to the direct B2-B19' transformation (Khalil-Allafi, 2006). This barrier results in opposing martensitic transformation, B2→R-phase that involves lower transformation strains (1–2%), becomes feasible and dominant. Further transformation occurs as R-phase converts to B19', resulting in two-step process that is seen as a double peak (two-stage) on the differential scanning Calorimetry (DSC) trace. Alongside, the large peak trace in DSC in the heating cycle indicates the B19'→B2 transformation occurred in one step. Yet, it was observed that aged Ni rich Ni-Ti alloys exhibited three DSC peaks during cooling from austenitic phase, instead of a two-stage transformation. Since the Ni-Ti alloy did not exhibit any competing martensitic transformation, other than to R-phase and B19' phase, there was uncertainty with regards to the correct interpretation of the multiple stage transformation (Wang, 2005).

(Bataillard), (L. Bataillard, 1998) observed that the transformation sequence of B2 matrix initially transforms to R-phase near the regions affected by the coherency stresses followed by the second transformation R-phase→B19'. The second transformation occurs in two steps, one near the precipitate and the other in the NiTi matrix volume unaffected by the coherency. Subsequently, (Allafi, 2002) have proposed that the 3-stage transformation was due to localized composition in homogeneity in the austenite due to the precipitation of Ni-rich  $\text{Ti}_3\text{Ni}_4$  precipitates that deplete Ni from the surrounding matrix, as shown in figure 2.48.



**Figure 1: Preferential Precipitation of  $\text{Ti}_3\text{Ni}_4$  Phases at the Grain Boundary (GB) and near the  $\text{Ti}_4\text{Ni}_2\text{O}$  in the Grain Interior (GI) after Aging for (a) 1hr, (b) 10hrs. Heterogeneous Precipitation Magnified near the Grain Boundary after Aging for (a) 1hr, (b) 10hrs.**

Literature also confesses that the transformation temperatures are highly sensitive to the Ni composition of the matrix, the composition (chemical) in homogeneity in the volume surrounding the precipitates would result in a single B2→R transformation followed by two R→B19' transformations taking place near and away from the precipitates, respectively (Carroll, 2004).

Recently, in situ TEM studies (Carroll, 2004) (Dlouhy, 2003) of multiple-step martensitic transformations in Ni-rich NiTi alloy suggested that the first DSC peak corresponds to the B2→R-phase transformation near the grain boundary (GB) followed by the R-phase→B19' transformation is due to the preferential precipitation of lenticular  $\text{Ti}_3\text{Ni}_4$  at the grain boundaries. Furthermore, the third peak then corresponds to the direct B2→B19' transformation in the precipitate free grain interior (GI) region. It is evident from the literature that the large scale in homogeneity in the microstructure due to precipitation near the grain boundary results in the Multiple Stage Transformation.

The above theories pronounce that the local-scale in homogeneity in either coherency stress fields or chemical composition, or the large-scale micro structural in homogeneity (due to preferential GB precipitation) show that the 3-stage

transformation is the norm rather than the exception. These papers also disclosed that the formation of micro structural inhomogeneity due to preferential precipitation in 3 stage transformation is not only because of the presence of grain boundaries but also due to the degree of super saturation, which is high in Ni-rich alloys such as 51.5-NiTi, that governs the nucleation kinetics of the  $Ti_3Ni_4$  precipitation. If the degree of super saturation is high the precipitation process is less sensitive to the presence of GB, and thus results in a homogeneous precipitation and yields only a 2-stage transformation whereas if the degree of super saturation is low, the precipitation is severely affected by the presence of grain boundaries (GB), since the GB nucleation rate is substantially greater than in the grain interior. This leads to large-scale heterogeneity in microstructure and chemical composition between the grain boundaries and the grain interior (Fan G. C., 2004). Thus, [4]– (Fan G. C., 2004) concluded that the two opposing factors, viz., presence of grain boundaries that initiates preferential precipitation due to favorable energetics and the Ni super saturation level that dictates the nucleation rate, govern the distribution of the precipitates and thus the nature of MST, i.e., 2-stage vs.3-stage.

### Review on Processing Parameters and Composition of Ni% in Ni-Ti Sma Models

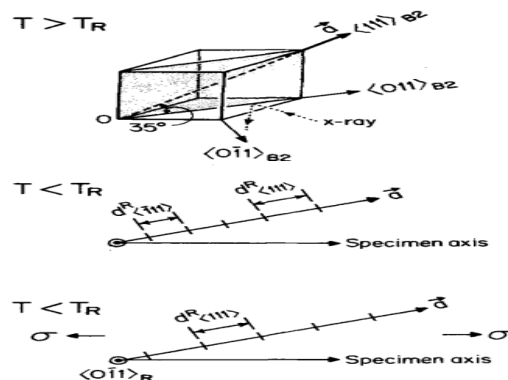
Models so far discussed are based on micro, macro and micro-macro approach with parameters such as martensite volume fraction, transition temperatures, energy dissipation, phase transformation, elastic strain and respective stress and loading conditions. But it is important that these all parameters are well established at near equiatomic composition. Very few in the literature have been cited about the composition and processing influence on properties of the SMA

At near equiatomic composition of Ni-Ti, first notable work was performed by (Hung C Ling, 1981), where author analyzed the importance of role of recoverable strain accommodation in R-phase during stress induced domain reorientation. The directional orientation of the recoverable strain is given by equation 1.

$$\frac{\Delta l}{l} = \frac{d_{(111)}^R - d_{ave}}{d_{ave}} \quad (1)$$

where,  $d_{ave} = (d_{(111)}^R + 3d_{(111)}^B)/4$  and  $d$  is deformation as given in the .

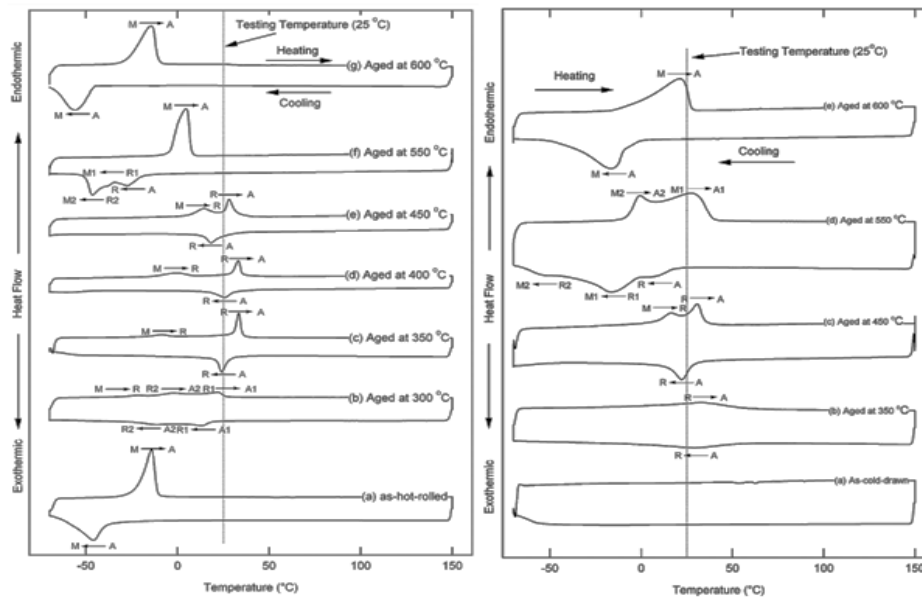
The paper lacks important concept of understanding strain as a macroscopic change during  $R \rightarrow B2$  transition. And in multiphase interaction, this situation becomes more complex if the R-Phase domain structure is unknown.



**Figure 2: Schematic of R-Phase Strain Accommodation during Tensile Straining.**

In this quandary, a solution suggested the influence of heat treatment was triggered during an experimental observation of R-Phase existence (Carl P. Frick, 2005). Examined hot rolled and cold drawn Ni-Ti SMA samples and observed that R-Phase transformation occurs in single and multi-stage phases for various aging

conditions. The following observations can be drawn from the DSC graphs of hot rolled and cold drawn specimens as shown in figure 3.



**Figure 3: DSC Graph of Hot-Rolled (Left) and Cold Drawn (Right) Ni-Ti Sma.**

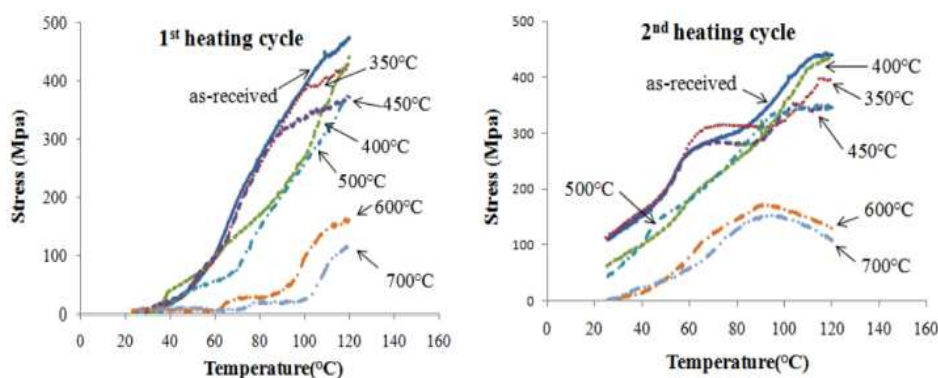
The following conclusion derived from the below graphs suggesting that

- For hot rolled samples, coherency and size of the precipitates directly influenced the transformation temperatures indicating various isothermal stress-strain behaviors in polycrystalline Ni-Ti SMAs.
- A similar trend is observed from the above for cold drawn but slight difficulty in determining transition temperature because of the large dislocation density.
- A hierarchy resulted from the observation which can be a work for future scope that hardness and martensite transformations are depicted as a function of heat treatment.

It is important to note the conditions which exhibit shape memory effect in Ni-Ti SMA as a function of heat treatment. From the literature review so far observed, none of the constitutive model speaks about the effect of heat treatment in their models. From the objective of our work it is very clear that a well posed constitutive model will be developed to include the composition and processing parameters as a phenomenological function. The following key points are observed from the literature on the works of heat treatment characteristics for Ni-Ti SMA from (Todoroki, 1987), (M. Nishida, 1988), (D.N. Abujdom, 1991), (Ken Gall H. S., 1999) and (Ken Gall H. S., 1999).

- SME is exhibited on the grounds of heat treatment process from the literature so far, that at different aging characteristics for equiatomic and rich Ni and Ti compositions were observed and found that rich Ni yields in precipitate growth.
- Aging influences both the process of dislocation annihilation (recovery for the duration of annealing) and precipitate growth. Aging heat treatment of a cold-rolled sheet material is in all likelihood to produce a complex micro shape containing incredibly large densities of dislocations and precipitates that are interwoven in such a way that precipitation can also take place mainly on dislocations, act as barriers for dislocation movement, and might also restrict the recovery process.

- It is also indicative that  $\text{Ti}_3\text{Ni}_4$  precipitates are observed during aging at specific temperatures for various processing methods (Carl P. Frick, 2005), it can be observed that for hot rolled and cold drawn, the DSC characteristics revealed almost similar phenomena but with little difficulty of tracing R-phase i.e.,  $\text{Ti}_3\text{Ni}_4$  precipitates due to large dislocation density.
- These large dislocation densities can be correlated to single crystalline and polycrystalline SMA samples through tensile test at room temperatures indicating the different failure phenomena in different planes (Ken Gall H. S., 1999). Hence cold drawn specimens exhibit a distinct behavior in single and polycrystalline Ni-Ti SMAs.
- During aging treatment, it is imperative to discuss the R-phase existence at different stages such as in between B2-M and M-B2 exhibiting multistage R-phase transformation.
- It is also revealing that the size of the precipitates influence triggering the martensite stress induced temperature.
- The precipitate size assumes a definitive role in deciding the yield strength and subsequently the yield strength diminished with increasing the aging time on account of the increased precipitate size. Moreover, the alloy with rich Ni owns low precipitate size and high volume fraction of  $\text{Ni}_4\text{Ti}_3$  precipitates, all of which contribute to a high yield strength (Fan Q. C., 2017).
- During annealing treatment, it is observed from (H Sadiq, 2010) that recovery stresses can be increased with increase in the pre-strain of the material. Alongside, at lower annealing temperatures with larger pre-strain, higher stress recovery can be ensued which is displayed in



**Figure 4: Maximum Recovery Stress at Different Annealing Temperatures. All the Samples are Pre-Strained to 4% Strain.**

- It is important concept that can be acknowledged from the paper is that annealing temperatures don't affect the transformation temperatures as shown in . From our understanding to clear the impasse in our objective, composition plays an important role in deciding the transformation temperatures. Emphasize will be made about compositional effect on material characteristics behavior.

It is important to note that there is a threshold annealing temperature and pre-strain values where the above points will be valid, reasonably this threshold region can be termed as R-phase region.

- It can be asserted by (Dalibor Vojtěch, 2011) from that after forming the precipitates during annealing at different temperatures for near equiatomic composition of Ni and Ti, there is a slight increase in tensile strength (almost linear variation) which is observed at the temperature ranging from 410°C to 450°C/2min/8min/16min.
- It is a well-known fact that recrystallization temperature for pure metals or alloys range from 0.3 to 0.5 times of melting point. This validation can be observed in that, apart from the existence of precipitates during B2-M, at certain aging time there are multi-stage R-phase transformations observed during M-B2. This is imperious just like the recrystallization temperatures for pure metals and alloys.

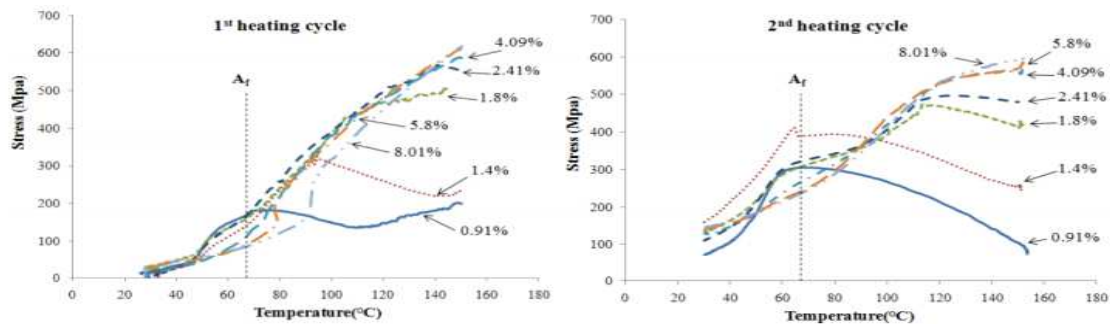


Figure 5: Recovery Stress for Ni-Ti Represented by Stress–Temperature Curves of Different Pre-Strains for the as-Received Wire.

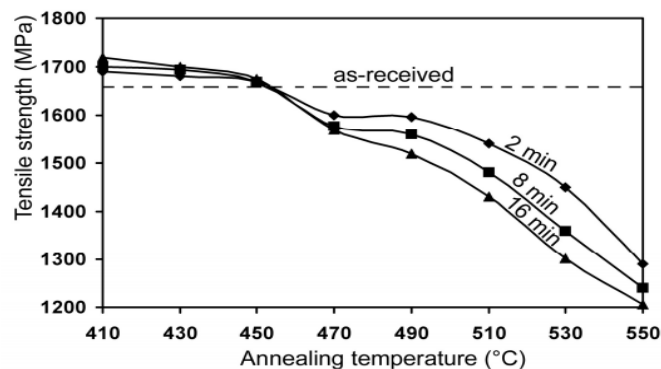


Figure 6: Development of Tensile Strength during 2, 8 and 16 Min Annealing at Various Temperatures.

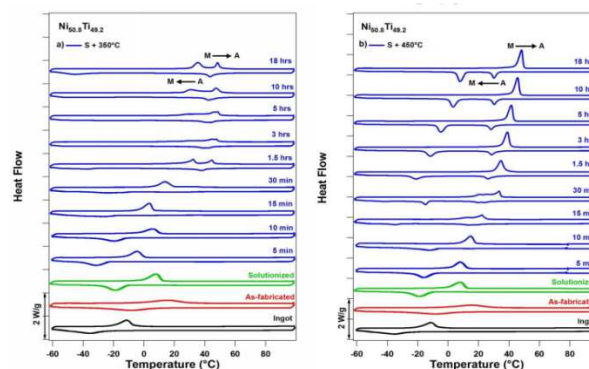


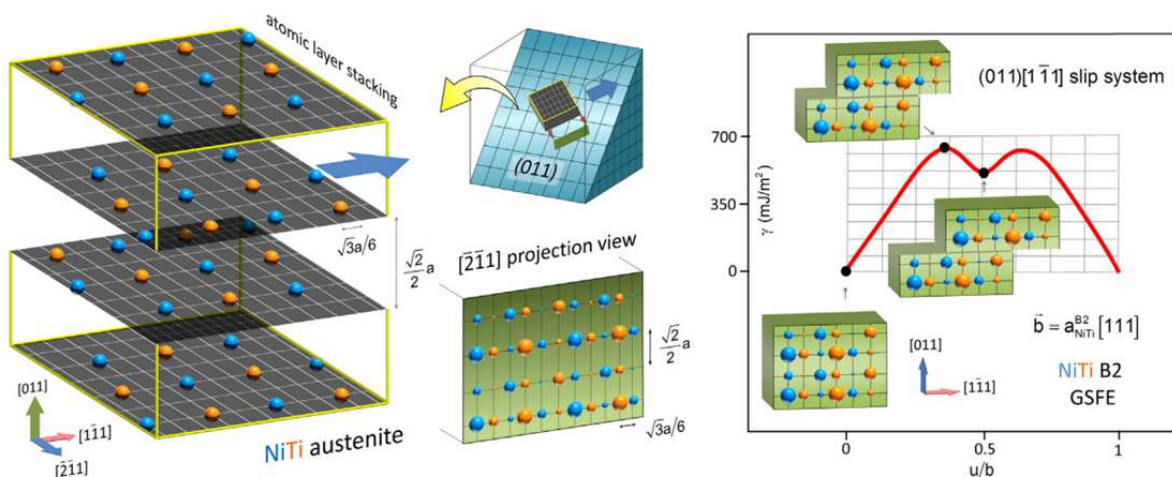
Figure 7: DSC Response of Solutionized SLM Ni50.8Ti49.2 Alloys Aged at a) 350°C b) 450°C as a Function of Aging Time.



## Review on Stacking Fault Energy Models

It is resilient to admit that the crystallographic defects show their influence in attaining different properties to the materials. In contrast to this, one such crystallographic defect which is usually observed in all conventional metals to recent smart materials is stacking fault. Stacking fault is a planar defect which interrupts the regular sequence of the atomic layers of the crystal structure. The energy per unit area of this stacking fault plane is called stacking fault energy (SFE). This SFE is so important in constructing a constitutive modelling at microscopic level since it changes as the composition of the alloy changes. From the literature, few points to be noted for the calculation of SFE of SMA are discussed below.

- Nickel and Titanium being the transition group elements, the influence of d-band structure on SFE is discussed in (I.R.Harris, 1966) and concluded that the presence of empty d-states largely increases SFE.
- Effect of alloy composition on SFE has been shown by (Jin Xuejun, 2000) based on thermodynamic calculations together with XRD profile on stacking fault density.
- During the development of microscopic constitutive models by different authors, (Otsuka, 1986) verbalized the importance of Stacking Fault Sequence as one of the transformation phenomena from  $B2 \rightarrow M$  which is associated with twins. But on the other hand, author realized that the contribution of this effect to total strain is small from the previous work (T. Saburi, 1982).
- During the quest for constructing atomistic energies, an impressive work propounded by (Piyas Chowdhury, 2016) aided in building the constitutive model. The terminology for stacking fault can be clearly understood for SMA's and an extensive investigations are discoursed which formed the elementary contributions to develop a profound model. An evidence of understanding the stacking sequence and slip can be visualized in the below figure 7.



**Figure 8: (Left) Schematic of the (011)  $[1 \bar{1} \bar{1}]$  Slip System and the Associated Atomic Stacking on the (011) Plane in NiTi Austenite. The  $[2 \bar{1} \bar{1}]$  Projected View is shown to Indicate in- and Out-of-Plane Atoms. Atoms of the Same Size (Either Ni or Ti) are on the Same  $[2 \bar{1} \bar{1}]$  Plane. (Right) the Corresponding GSFE Profile (Adapted from [27]) with Insets Showing the Atomic Positions during Shearing. The Existence of an Energy Saddle point Indicates a Strong Likelihood of Planar Fault Formation in Conjunction with Slip.**

- [28] Envisioned propagation of twin boundaries during the application of tensile load can be studied from Centrosymmetric parameter [29] which is used to measure the local atomic coordination which indicates bulk, fully

coordinated atom while increasing values indicate lattice defects such as stacking fault and twins. The dislocations of the atoms using the SFE by the critical shear stress as a function of thermal and mechanical loading conditions at third stage of strain hardening. These strain rate dependent parameters are well defined by [30].

### Research Gaps Identified from the Literature Review

The following research gaps are identified from the literature review.

- It is observed from the literature that, most of the constitutive models developed so far are for near equiatomic compositions. However, few models exist but are not practically justified because of the rigorous behavior of this alloy which involves too many parameters in understanding the SME. More precisely speaking, author is expected to understand the SME as a function of individual parameters at different compositions.
- Literature cites not only the composition but also SME depends on material processing parameters. Most importantly, understandings of these parameters are done for near equiatomic compositions through different manufacturing routes.
- Since SMA phase diagram comprises of stress–strain–temperature hysteresis, most of the constitutive models available so far are energy based microscopic models. Recent developments to these models include most of the atomistic data in a very decent way besides increasing the complexity of the mathematics. To surmount this complexity, an optimized micro-macroscopic model should be constructed which reduces the number of parameters by using a suitable statistical method.
- Prediction of hysteresis behavior of nitinol alloys is one of the challenging aspects that have received substantial attention as a future scope in many articles. But a very trivial amount of literature is available, so there is a need to examine the hysteresis behavior with compositional variation.
- While the past studies provide a consistent explanation for all the features observed in DSC experiments, further work is required to describe the microscopic details of two and multiple step martensitic transformations as they evolve with ageing time. It is also important to consider the possible influence of other microstructural inhomogeneities such as a heterogeneous distribution of particles in the microstructure.
- Most of the exciting work on SMA is mostly available in framework to biomedical applications because of its biocompatible nature. The mechanical properties of these materials possess are amenable to bio-industry. But its exciting properties of SME have a potential demand in aerospace and automotive industries. But, due to the lack of other properties such as high strength to weight ratio, thermal resistance etc., and these alloys have become a current area of research. Though microscopically ample amount of understanding is available in the literature, number of parameters involved with SME has become one of the challenging problems to the scientists and engineers. Hence, parameters influencing these properties required by industries (aerospace and automotive) without upsetting the SME need to be examined.

### CONCLUSIONS

Nitinol SMAs despite receiving ample attention haven't been explored towards diverse applications because of their processing difficulties and demand of physical properties by different industries. In this context, an understanding for



processing parameters gives a full insight of these alloys to explore to various industries mostly aerospace and automotive industries. This enables the scientific community to focus on specific parameters that are very vital in modelling the SMA.

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## AUTHORS PROFILE



**Mudavath Baburam:** Graduate student in the branch of Mechanical Engineering from Chaitanya Bharathi Institute of Technology, (Osmania University) Gandipet, Hyderabad, Telangana State, India 500075. He is a young research scholar in the field of Advanced Material Science.



**Dheeraj K Gara:** Holds a position of Deputy Director for Vsky aerospace technologies; he has published few research articles in the areas of material sciences. He is expertise in processing and modeling of shape memory alloys, structural health monitoring of mechanical systems. He is also pursuing PhD from NIT Rourkela in Mechanical Engineering.



**K Damodhar:** Is a research fellow at Research center Imarath, DRDO Hyderabad. He is expertise in modeling of advanced material sciences especially in nitinol shape memory alloys. He is graduate in mechanical engineering from Chaitanya Bharathi Institute of Technology, Hyderabad.



**K Gurubrahmam:** Assistant professor in the department of mechanical engineering at the Chaitanya Bharathi Institute of Technology (CBIT), Hyderabad, where he has been a faculty since 2016. His specialization and research interests are in the areas of Mechanical vibrations & Acoustics, condition monitoring, Structural mechanics, Smart Structures, Experimental Modal analysis, digital signal processing and instrumentation. At CBIT Hyderabad he teaches Dynamics of machines, Mechanical vibrations, production drawing, machine design.

